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Effect of relaxation state on nucleation and grain growth of nanoscale quasicrystal in Zr-based bulk metallic glasses prepared under various cooling rates

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$Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ bulk metallic glasses (BMGs) in various relaxation states were prepared under different cooling rates. The grain growth rate of the primary quasicrystal was examined near the crystallization temperature. It was approximately 1×10^{-9} m/s in less relaxed BMGs and approximately twice as large in relaxed BMGs. In contrast, the calculated homogeneous nucleation rate of the less relaxed samples was five to ten times higher (5×10^{19}–1×10^{20}/m^{3}s) than those in the relaxed BMGs. The results indicate that the relaxation state of glassy alloys has a marked effect on nucleation and grain growth behaviors. © *2011 American Institute of Physics*. [doi:10.1063/1.3622117]

Bulk metallic glasses (BMGs) are currently recognized as one of the most attractive fields of material science. They have been widely studied with great interest owing to their good mechanical, chemical, and magnetic properties.[1] In order to overcome the major concern of the low ductility of BMGs, control of the nano structure as well as the alloy design has, usually, been applied.[2,3] Recently, it has been found that the relaxation state of glassy alloys is also an important factor affecting the ductility. Kumar *et al*. have reported that the embrittlement of Zr-based BMGs can be reversed by substantially annealing for a short duration above the glass transition temperature, T_g (so-called recovery annealing).[4] They investigated that the recovered ductility is correlated with the structural relaxation behavior in the glassy structure. The relaxation of BMGs annealed at low temperatures of around or below T_g has attracted great attention in terms of its effect on properties such as the local structure,[5,6] thermodynamics,[7–10] and crystallization.[11,12] Very recently, the authors have reported the effect of the chamber atmosphere on the structure and properties of BMGs prepared by the Cu mold casting technique.[13,14] We found the enhancement of the cooling effect when the alloy melt is cast in an Ar or He atmosphere rather than in vacuum,[15] leading to the production of BMGs with various relaxation states by controlling the chamber atmosphere. Actually, we have produced less relaxed (unrelaxed) Zr-Al-Ni-Cu-Pd BMGs with improved compressive room-temperature ductility.[16]

Thus, the structural relaxation of BMGs is recognized as one of the important phenomena with a considerable effect on their mechanical properties. Generally, we have to use BMGs with various relaxation states for industrial applications which originate from different production methods and conditions. However, little is known about the effect of the relaxation state on the fundamental kinetics of transformation behavior such as nucleation and grain growth in BMGs. In this letter, we investigate the change in the nucleation and grain growth rates of the primary quasicrystalline (QC) phase[17] quantitatively in $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ BMGs with different relaxation states. Such fundamental information will be useful for controlling the structure of BMGs through the precipitation of nano particles by annealing for the purpose of improving the mechanical properties.

$Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ bulk glassy samples with 3 mm diameter were produced by the Cu mold casting technique under various Ar and He pressures, in addition to a vacuum atmosphere. The cooling rate was monitored by a thin K-type thermocouple connected to an analog-to-digital converter. The relaxation state of the glassy structure was evaluated by the enthalpy of relaxation, calculated from the results of a specific heat measurement, with a heating rate of 0.33 K/s, under a purified Ar flow using a differential scanning calorimetry (DSC) (Perkin-Elmer Pyris Diamond DSC). The structure of the samples was analyzed by X-ray diffraction (Cu-Kα, 40 kV-40 mA) and high-resolution transmission electron microscopic (TEM) observation (JEOL JEM 3000F). Glass transition (T_g) and crystallization (T_x) temperatures were determined by DSC measurements. The grain growth behavior of the annealed samples was directly observed using a TEM.

We have previously reported that the cooling rate of a supercooled liquid at low temperatures ($\sim T_g + 160$ K) can be changed significantly by controlling the chamber atmosphere.[16] Moreover, we proposed that the dominant factor determining the relaxed state in glassy alloys is the cooling rate at the above low temperatures, where each atom is fixed in its final position owing to the low mobility, resulting in a variety of relaxation states depending on the cooling rate. Figure 1(a) shows the relationship between the cooling rate just above T_g and the enthalpy of relaxation ΔH_{relax} in the production of $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ BMGs. ΔH_{relax} can be obtained by the following equation:[18]

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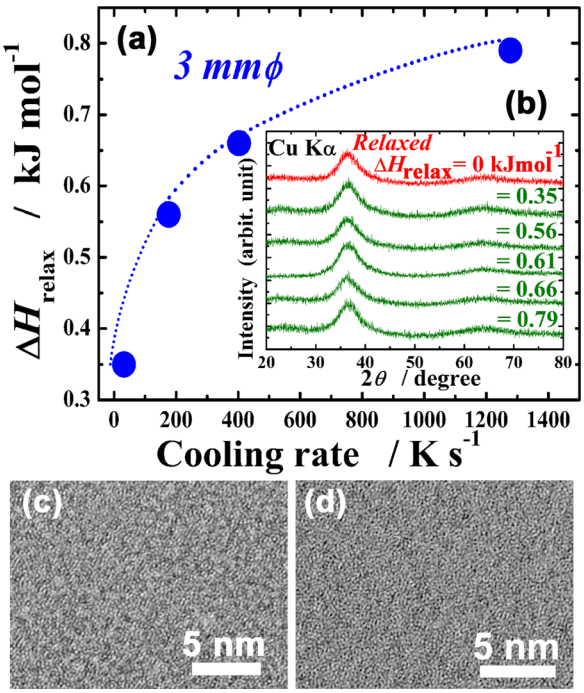

FIG. 1. (Color online) Relationship between the cooling rate just above glass transition temperature T_g and the enthalpy of relaxation ΔH_{relax} (a). X-ray diffraction patterns of as-cast BMGs with various enthalpies of relaxation ΔH_{relax} (b). Data of relaxed sample (BMG with $\Delta H_{relax} = 0.66$ kJ/mol annealed for 60 s at 655 K) is also denoted in (b). High-resolution TEM images of the as-cast (c) and annealed (655 K-60 s) (d) samples with $\Delta H_{relax} = 0.66$ kJ/mol.

$$\Delta H_{relax} = \int_{RT}^{Tg} \Delta C_p (= C_{p,s} - C_{p,q}) dT, \quad (1)$$

where $C_{p,s}$ and $C_{p,q}$ are the specific heats of the relaxed and as-prepared states, respectively. The results clearly indicate the strong relationship between them, in which ΔH_{relax} increases monotonically with increasing the cooling rate. The BMG shifts to a significantly less relaxed state with increasing cooling rate. The least relaxed state with $\Delta H_{relax} = 0.79$ kJ/mol is achieved at a cooling rate of 1280 K/s in the present study. These BMGs with various relaxation states have similar XRD patterns, as shown in Fig. 1(b). All of them have only broad halo peak without any diffraction peaks. Similar glassy pattern is observed even in an almost fully relaxed state ($\Delta H_{relax} \approx 0$ kJ/mol) prepared by annealing the sample with $\Delta H_{relax} = 0.66$ kJ/mol for 60 s, just above T_g (655 K). The typical high-resolution TEM images of the as-cast sample with $\Delta H_{relax} = 0.66$ kJ/mol and its relaxed state are shown in Figs. 1(c) and 1(d), respectively. Both images reveal the homogeneous microstructure and no obvious ordered clusters and/or nanocrystalline particles contain. Due to the similar microstructure obtained in other BMGs, we can conclude that the present BMGs have a monolithic glassy structure. Actually, the measured T_g and T_x are 650 K and 722 K, respectively, within the accuracy of ±2 K in all the as-cast samples.

Figure 2 shows bright-field TEM images of the primary QC particles in BMGs with different relaxation states, after annealing at 720 K for various annealing times (18 – 42 s). The results of an almost fully relaxed state are also denoted in the figure. It is clear that different growth behaviors are

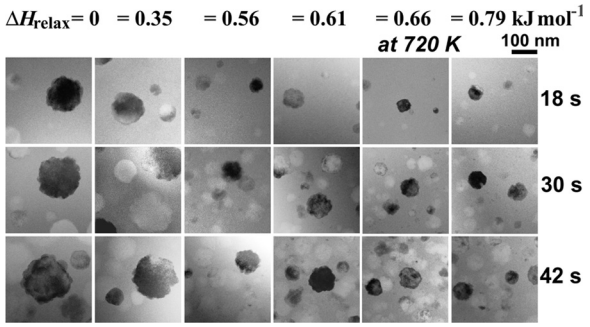

FIG. 2. Bright-field TEM images of the primary QC particles in BMG samples with different relaxation states annealed at 720 K ($\approx T_x$) for various annealing times. The results for an almost fully relaxed state ($\Delta H_{relax} \approx 0$ kJ/mol), in which the sample is annealed for a short time (approximately 60 s) just above T_g, are also denoted in the figure.

exhibited depending on the relaxation state. The QC particles grow faster in more relaxed samples ($\Delta H_{relax} = 0$ and 0.35 kJ/mol) than in the less relaxed samples. For example, the maximum size of QC particles for the annealing time of 30 s is 170 nm at $\Delta H_{relax} \approx 0$, 150 nm at $\Delta H_{relax} = 0.35$ kJ/mol, 94 nm at $\Delta H_{relax} = 0.56$ kJ/mol, and 82 nm at $\Delta H_{relax} = 0.66$ kJ/mol. The primary QC particles nucleate homogeneously and grow with an isotropic morphology. A phase transformation with an isotropic constant is expressed by the following equation, in terms of the isothermal annealing time t_a:[19]

$$X = 1 - \exp\left(-\frac{\pi I_v u^3 t_a^4}{3}\right), \quad (2)$$

where X is the volume fraction transformed. I_v and u are the homogeneous nucleation and grain growth rates, respectively. From Eq. (2), we can calculate the homogeneous nucleation rate I_v as follows:

$$I_v = -\frac{3}{\pi u^3 t_a^4} \ln(1 - X). \quad (3)$$

The change in u, calculated from the maximum size of QC particles, with ΔH_{relax} is revealed as the solid square (■) in Fig. 3(a). A strong correlation between the grain growth rate and the relaxation state is observed in the figure, in which u is markedly decreased with increasing ΔH_{relax}. The growth rates in the relaxed glasses at $\Delta H_{relax} \approx 0$ and 0.35 kJ/mol, for example, are 2.9×10^{-9} and 2.3×10^{-9} m/s, respectively, which are approximately twice as high as those in the less relaxed BMGs (1.8×10^{-9} m/s at $\Delta H_{relax} = 0.56$ kJ/mol and 1.2×10^{-9} m/s at $\Delta H_{relax} = 0.66$ kJ/mol). Since the macroscopic structure is almost the same for the relaxed and less relaxed BMGs, the difference of the grain growth rate might originate from the transition of the local structure at different cooling rates. This suggestion implies a change of the nucleation behavior of the primary QC phase with the relaxation state. I_v at 720 K in the steady state of $X = 0.2$, calculated from Eq. (3), is also plotted for the BMGs with various relaxation states as the solid circle (●) in Fig. 3(b). It is found that the calculated I_v has a significant correlation with the relaxation state, in which it increases with increasing ΔH_{relax}. I_v is 4.1×10^{18}/m^{3}s in the almost fully relaxed sample ($\Delta H_{relax} \approx 0$) and increases to 5.1×10^{19}/m^{3}s at $\Delta H_{relax} = 0.66$ kJ/mol and

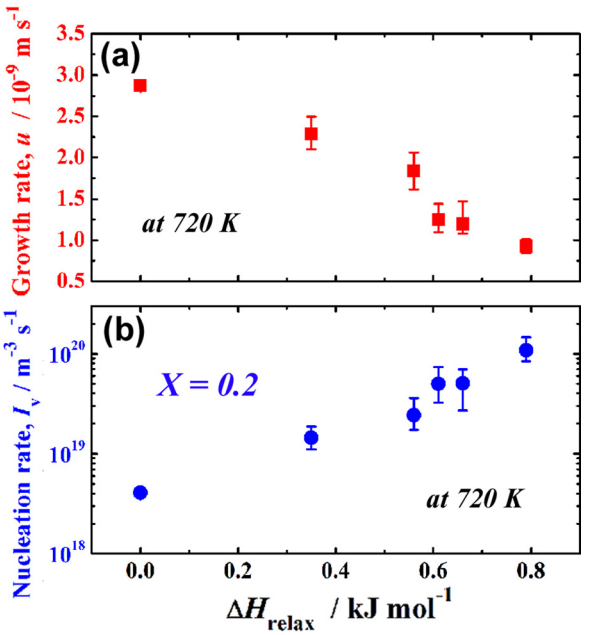

FIG. 3. (Color online) Change in the grain growth rate (a) at 720 K, measured from the maximum size of QC particles, and the calculated I_v (b) in the steady state of $X = 0.2$ with the enthalpy of relaxation ΔH_{relax}.

1.1×10^{20}/m^{3}s at $\Delta H_{relax} = 0.79$ kJ/mol. Actually, the observed TEM images in Fig. 2 indicate the precipitation of more QC particles with a smaller size in the less relaxed samples than in the relaxed samples. The tendency is in contrast to the relation between the grain growth rate and the relaxation state.

The structural change in BMGs during relaxation has been studied by various methods.[6,20,21] It was investigated that metallic glasses with a higher cooling rate have a smaller fraction of full icosahedra. During the relaxation process induced by annealing below T_g, the fraction of full icosahedra increases. Additionally, it was pointed out that chemical ordering is enhanced in the relaxed state. Meanwhile, the growth mechanism of QCs in the glassy structure has also been investigated.[22] Mechler *et al.* have reported that the formation of QC from the amorphous phase is determined by the rearrangement of the icosahedral clusters rather than by the attachment of single atoms.[23] The results of molecular dynamics simulations have indicated that there is an increased presence of icosahedral clusters surrounding the QC nucleus. Furthermore, icosahedral clusters would like to "wet" the core of the QC nucleus owing to the reduction of interfacial tension.[24] These clusters change the connectivity to ordered QC arrangements as the nucleus grows.

On the basis of these studies, BMGs prepared at a low cooling rate or in the relaxed state contain a limited number of ordered or grown QC nuclei, which might be equivalent to the chemical ordering discussed in Ref. 20. Consequently, it results in easy grain growth (i.e., a high growth rate) with a low nucleation rate. In contrast, considerably fewer ordered QC nuclei are present in less relaxed BMGs formed at a high cooling rate, preventing growth at these nucleation sites. In such a case, QCs have to grow from relatively disordered or an insufficient number of nuclei before the aggregation of related icosahedral clusters, which provide an opportunity for nucleation at many locally ordered regions (i.e., a high nucleation rate). This also results in difficult QC growth (a low growth rate) owing to the attachment of few clusters.

In the present study, we have found that the relaxation state strongly correlates to the nucleation and grain growth rates of the primary QC phase in $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ BMGs. The relaxed BMGs have lower nucleation rates and higher growth rates than the less relaxed BMGs. We suggest that this is due to the different state of the primary QC nucleus for a different relaxation state. A relaxed BMG has a considerably ordered or grown nucleus, which is formed by the aggregation of surrounding icosahedral clusters, leading to the easy growth from the limited number of sites. In contrast, nucleation frequently occurs from the other insufficient sites owing to the lack of such ordered or grown nuclei in less relaxed BMGs, resulting in high nucleation and low growth rates. Finally, the present results reveal the importance of controlling the relaxation state during the formation of nanostructures in BMGs and provide useful information for it.

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